

## NO DRAWINGS

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(54) METHOD OF INCREASING POLYMER MOLECULAR WEIGHT AND INTRODUCING TERMINAL GROUPS

(71) We, THE INTERNATIONAL SYNTHETIC RUBBER COMPANY LIMITED, a Company organised under the laws of Great Britain, of Brunswick House, Brunswick Place, Southampton, Hampshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This application relates to a process for preparing polymers of increased molecular weight. In another aspect it relates to a process for preparing polymers with specific end groups.

As is well known, many organometallic catalysts will polymerise conjugated dienes and copolymerise them with activated vinyl compounds. Thus, *n*-butyl lithium will polymerise 1,3-butadiene and copolymerise 1,3-butadiene with styrene to high molecular weight rubbery polymers. The mechanism is generally considered to be anionic, i.e. the growing chain end may be described by the simplified, generalised formula:—



where  $R^-$  is the organic chain and  $M^+$  is the inorganic counter ion.

Large amounts of cheap extenders such as oil and carbon black may be added to these high molecular weight polymers without lowering the physical properties of the compounded rubbers below an acceptable level. The higher the molecular weight of the polymer, the more extender can be added to cheapen the overall cost of the final rubber compound and yet maintain the desired properties.

On a large scale, there are considerable problems in producing polymers with Mooney Viscosity ( $ML_{1+4}^{100^\circ C}$ ) above about 60. The molecular weight as estimated by Mooney Viscosity is controlled by catalyst/monomer ratio. The smaller this ratio, the higher the molecular weight of the polymer. To produce

rubbers with Mooney Viscosity of 100, very low levels of catalyst are required and at these levels the normal impurities in the monomer feed are quite often sufficient to react with and deactivate the catalyst. Hence, direct polymerisation is difficult to control when very high molecular weight polymers are required.

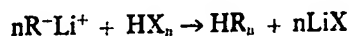
Another problem in producing high molecular weight polymers concerns the bulk viscosity of the reaction medium. The polymerisations are usually carried out in an inert solvent and to minimise the solvent and monomer recycle and hence to improve the economics of the process, the polymerisation is carried out to the highest conversion and to the highest polymer content possible. However, most conventional pumping and stirring units will not cope efficiently with polymer solutions having bulk viscosities in excess of about 10,000 cps. Unfortunately, at a given polymer content of the solution, the bulk viscosity increases sharply with the molecular weight of the polymer. For example, polybutadiene solutions of 15% solids in hexane have bulk viscosities at different polymer Mooney viscosities as follows:— 1,000 cps at 20 Mooney, 10,000 at 50 Mooney and 50,000 at 100 Mooney.

It would obviously be advantageous to prepare lower molecular weight polymers by direct polymerisation and to increase the molecular weight in a subsequent step.

According to the invention there is provided a method for increasing the molecular weight of conjugated diene polymers or copolymers prepared from monomers containing not more than 0.2% by weight of acetylenic or allenic impurities by means of an organometallic catalyst containing a metal of Group IA or IIA of the Periodic Table, comprising adding to the live polymerisation system one or more heteroaromatic compounds each containing at least one labile atom or group, as hereinafter defined, the molar ratio of the heteroaromatic compound to the organometallic catalyst lying within the range 0.01—

10. The Periodic Table referred to throughout this Specification, including the Claims, is the one set out on page 30 of "Advanced Inorganic Chemistry" by F. A. Cotton and  
5 G. Wilkinson published by Interscience Publishers (1962).

Whilst it is not intended to limit the process of the invention to any particular mechanism, it is believed that the "live" polymer chains couple together in the following  
10 manner:—



where  $R-Li^+$  is the terminally active chain as hereinbefore defined,  $HX_n$  is the hetero-aromatic compound containing the labile  
15 atom(s) or group(s) X and n is an integer. The reaction is very fast and liberates very little sensible heat.

If the "live" polymer chains are reacted  
20 with heteroaromatic compounds containing more than one labile atom or group (i.e. n in the reaction above is 2 or more) the molecular weight of the polymer shows a marked increase. On the other hand, if the active  
25 polymer chains are reacted with heteroaromatic compounds containing one labile atom or group only, (i.e. n = 1 in the above reaction), then new products of slightly increased molecular weight may be synthesised having pre-determined end groups. Such end groups may  
30 be used for further reaction or may, depending on their nature, confer acidic or basic character on the hydrocarbon polymers thus facilitating bonding to fibres, dyeability, etc.  
35 This is of particular advantage where the catalyst is difunctional and promotes growth of the polymer chain at both ends, as an end group may be inserted at each end rather than at one end.

The conjugated diene monomers which may be polymerised to produce live polymer chains are well known in the art. Preferred monomers are those containing 4 to 8 carbon atoms in the main chain for example 1,3-butadiene,  
45 isoprene, piperylene, methyl pentadiene, phenyl butadiene, 2-chloroprene. Particularly preferred are butadiene and isoprene. It will be understood that any combination of such dienes may be used. Polymerisable vinyl compounds such as styrene, vinyl naphthalene,  
50 vinyl anthracene, vinyl toluene and vinyl xylene may be copolymerised with such dienes, as is well known. Generally, the percentage by weight of such comonomers, based on the total weight, is 50 or less, normally from 10%  
55 to 30%. In some circumstances, however, up to about 80% may be used.

Catalysts suitable for use in the polymerisation are organometallic compounds from  
60 Groups IA and IIA of the Periodic Table. These are of the 'anionic' type and are well known in the art. Examples are n-butyl lithium, phenyl lithium, benzyl lithium, di-

lithium naphthyl, isopropyl potassium, phenyl sodium, diethyl magnesium, and diethyl beryllium. Others normally considered to operate by anionic mechanisms, such as lithium butyl in admixture with ethers and polyethers are  
65 equally suitable.

The amount of catalyst used for the initial polymerisation will depend on the molecular weight of the polymer which is required, as mentioned above, and is normally in the range 0.01—10 parts per hundred parts of monomer by weight. The preferred range is 0.01—  
70 1 part per hundred parts of monomer.

The initial polymerisation may be carried out at  $-100^\circ$  to  $+150^\circ\text{C}$  but more usually  $-10^\circ$  to  $+100^\circ\text{C}$  and at pressures between atmospheric pressure and 50 atmospheres.  
80

The heteroaromatic compounds suitable for use in the present invention contain at least one labile atom or group i.e. one which is readily displaceable, either  $\alpha$ - or  $\beta$ - (or in an equivalent position, i.e. a position from which charge delocalisation to the hetero atom can occur, in an adjacent aromatic ring) to a hetero atom which is contained in a hetero-aromatic ring. By aromatic, we mean those compounds which contain  $(4n + 2)$   $\pi$ -electrons where n is nought or an integer. Usually there are 6  $\pi$ -electrons e.g. as in pyridine, pyrrole, but compounds with 10  $\pi$ -electrons are common. More than one hetero atom may be present and this is frequently advantageous since the groups are thereby rendered even more labile. Examples of such labile atoms and groups are, halogen, alkoxy, aryloxy, *tert*-amine and cyanide groups. Halogen atoms are preferred.  
90 95 100

Heteroaromatic compounds containing nitrogen and/or oxygen and/or sulphur as hetero atom(s) are the most common and for this reason are preferred. Examples of such heteroaromatic compounds suitable for use in the invention are 2,4,6-trichloropyridine, 2,4,6-tribromopyridine, 2,4,6-triethoxypyridine, 2,4,5-tribromoquinoline, 2,4,6-triiodopyridine, 1,3,6-tribromoisoquinoline, 3,4,5-trichloropyridazine, 2,4,6-trichloropyrimidine, 2,3,6-triethoxypyrazine, 2,5,6-tribromopyrazine, 2,3,6-trichloroquinoxaline, cyanuryl chloride (2,4,6-trichlorotriazine-1,3,5), 2,4-dichlorothiazole, 2,4,5-trichloroimidazole, 2,5-diiodofuran and such compounds having only one labile group, e.g. 2-chloropyrimidine, 2-bromopyrazine, 2-chlorothiazole.  
105 110 115

The amount of heteroaromatic compound added should be in the range 0.01 to 10 molar equivalents based on the catalyst used in the polymerisation. For maximum molecular weight increase, the number of labile atoms or groups added should equal the number of live chains. Preferably the molar ratio of heteroaromatic compound to organometallic catalyst  
120 125 is substantially  $\frac{m}{n} : 1$  where m is the number

of metal-to-carbon bonds and  $n$  is the number of labile atoms or groups present in the heteroaromatic compound. For example, in the case of trichloropyridine or cyanuryl chloride (three labile atoms per molecule) added to a butyl lithium polymerisation system, the molar ratio additive/active butyl lithium = 0.33. Since some butyl lithium reacts with impurities often present in conjugated diene monomers (e.g. allene, acetylene), the most active range for additive/total butyl lithium is in the range 0.2—0.3 depending on the purity of the conjugated diene.

In the case of preparation of terminally active polymers prepared from mono-anionic compounds e.g.  $n$ -butyl lithium, clearly only one labile atom or group per polymer chain is required and thus the molar ratio additive/total catalyst should ideally be in the range 0.9—1.0 depending on the purity of the monomers.

For the invention to be carried out, the hetero-aromatic compound(s) are added to the live polymerisation system i.e. to the terminally active polymer solution. Normally the addition is made after a conversion to polymer of approximately 80%, preferably 90% or more, has been obtained, there being no advantage in making the addition earlier. Reaction is very fast, no special conditions being required. It is not necessary to heat the live polymer for long periods at high temperatures in the presence of the heteroaromatic compound it being quite sufficient to maintain the system at the temperature used for the polymerisation.

It is important for this invention to be effective that compounds which are known to reduce considerably the activity of the polymer chains be kept to a minimum. Thus such classes of compounds as allene, substituted allenes and alkynes should be kept within the range 0—2000 ppm by weight of the diene monomer, preferably below 500 ppm.

Low molecular weight rubbers, especially polymers and copolymers of butadiene, isoprene and piperylene having Mooney viscosities below 30, when prepared by direct polymerisation have a tendency to cold flow, making handling and storage difficult. An additional advantage of the present invention is that it enables such low molecular weight polymers having little, if any, tendency to cold flow to be prepared.

The following Examples illustrate the invention:—

#### EXAMPLE 1

The polymerisation of butadiene was conducted in a 1 pint crown-capped glass pressure bottle. The bottle was dried at 200°C/760 mm for 16 hrs. The bottle was well flushed with anhydrous, oxygen-free nitrogen (45 min) and fitted with a crown cap. The gaskets used in the cap were of the polychloroprene type which had been washed under

hexane and then pumped out at 60°C/10 mm for at least 24 hrs. before use.

50g dry 1,3-butadiene (containing 20 ppm 1,2-butadiene by weight as the principal harmful impurity) was condensed into the bottle by cooling it to -40°C. Then 220 ml. pure, dry hexane was added to the bottle. The bottle and contents were allowed to warm up to room temperature and  $n$ -butyl lithium (0.09 parts per hundred parts of monomer by weight) was added by syringe as a 1% w/v solution in hexane.

The bottle was placed in a wire cage and then into a bottle rotating machine in a water bath at 50°C (125°F) and the reaction allowed to proceed for 6 hrs.

At the end of that time the reasonably mobile polymer solution was a pale yellow colour. The bottle was withdrawn and cyanuryl chloride (such that the molar ratio cyanuryl chloride/ $n$ -butyl lithium was 0.33) was added by syringe as a 0.5% w/v solution in dry benzene. The bottle was placed back in the bottle rotating machine and the contents were allowed to mix and react for a further 1 hour at 50°C (125°F).

A solution of 0.5 g. 2,2' - methylene bis (4 - methyl - 6 - tert - butyl phenol) ["2,2,4,6"] antioxidant in 40 ml hexane (1 part per hundred parts of rubber) was added to the bottle and the contents agitated. The bottle was then opened and the rubbery product was worked up by pouring the contents into excess methanol. The product from the experiment, 49g (98% conversion) had a Mooney Viscosity, ML<sub>1+4</sub><sup>100°C</sup> 62.

A corresponding 'blank' experiment which was identical in every way, except that no cyanuryl chloride was added, gave a rubber with a Mooney Viscosity, ML<sub>1+4</sub><sup>100°C</sup> 10.

The microstructure of both polybutadiene rubbers, as measured by infrared spectroscopy according to the method of L. Hampton, Analytical Chemistry 1949, 21, 923, was 42.7% cis 1,4, 48.5% trans 1,4 and 8.8% 1,2 (vinyl). The gel content was < 0.1% w/w.

#### EXAMPLE 2

A similar procedure to that used in Example 1 was used except that the comonomers used were butadiene (30g) and styrene (10g) and the catalyst employed was  $n$ -butyl lithium (0.09 phm parts per hundred parts of monomer) and diglyme (diethyleneglycol dimethyl ether), such that diglyme/butyl lithium = 0.1 molar.

The resultant rubber had Mooney Viscosity ML<sub>1+4</sub><sup>100°C</sup> 40. A similar experiment without the cyanuryl chloride addition gave a rubber with Mooney Viscosity ML<sub>1+4</sub><sup>100°C</sup> 12.

The rubber in each case was a random co-

polymer containing no long blocks of polystyrene (as shown by chemical degradation) and the microstructure of the butadiene portion was cis 1,4 37%, trans 1,4 28%, 1,2 (vinyl) 35%.

#### EXAMPLE 3

The procedure used was similar to that given in Example 1 except that 2,4,6-trichloropyrimidine was used in place of cyanuril chloride. The rubber produced had Mooney Viscosity  $ML_{1+4}^{100^{\circ}C}$  55 and microstructure 42.1% cis 1,4, 48.0% trans 1,4 and 9.9% 1,2 (vinyl).

#### EXAMPLE 4

The procedure used was similar to that given in Example 2 except that 2,4,6-trichloropyrimidine was used in place of cyanuril chloride. The rubber was a random copolymer having no long blocks of polystyrene. It had Mooney Viscosity  $ML_{1+4}^{100^{\circ}C}$  35 and the butadiene portion had the microstructure cis 1,4 37.3% trans 1,4 28.8% 1,2 (vinyl) 33.9%.

#### EXAMPLE 5

A procedure similar to that of Example 1 was used except that isoprene was employed instead of butadiene.

The resulting polymer (47g) had a Mooney Viscosity  $ML_{1+4}^{100^{\circ}C}$  80 compared with a "blank" experiment where no cyanuril chloride was used which gave a Mooney Viscosity  $ML_{1+4}^{100^{\circ}C}$  22. The microstructures of both rubbers were similar and shown, from their infra red spectra by comparison with natural rubber and gutta percha standards, to be cis 1,4 80%, trans 1,4 12%, 3,4 8%, 1,2 0%.

#### EXAMPLE 6

A procedure similar to that of Example 1 was used except that 2,4,6-trichloropyridine was substituted for cyanuril chloride.

The polybutadiene rubber (40g) had Mooney Viscosity  $ML_{1+4}^{100^{\circ}C}$  45 compared with an equivalent "blank" experiment (no trichloropyridine) which had Mooney Viscosity  $ML_{1+4}^{100^{\circ}C}$  17.

#### EXAMPLE 7

A procedure similar to that of Example 1 was used except that 2,3,6-triethoxypyrazine was substituted for cyanuril chloride. The polybutadiene rubber (42g) had Mooney Viscosity,  $ML_{1+4}^{100^{\circ}C}$  53 compared with an equivalent "blank" experiment (no triethoxypyrazine) which had Mooney Viscosity  $ML_{1+4}^{100^{\circ}C}$  12. The microstructures of the rubbers were as in Example 1.

#### EXAMPLE 8

A procedure similar to that of Example 5 was used except that 2,4-dichlorothiazole was substituted for cyanuril chloride. The thiazole did not terminate the chains in the way expected of most sulphur compounds but it increased the molecular weight of the polymer. The Mooney Viscosity of the polyisoprene rubber was  $ML_{1+4}^{100^{\circ}C}$  51 compared with a "blank" of  $ML_{1+4}^{100^{\circ}C}$  18 when no additive was present. The microstructures were as for Example 5, i.e. of the "medium cis" type.

#### EXAMPLE 9

A procedure similar to that of Example 1 was used except that 2,5-diiodofuran was substituted for cyanuril chloride. The Mooney Viscosity of the polybutadiene rubber was  $ML_{1+4}^{100^{\circ}C}$  49 compared with the "blank" experiment (no furan) which gave  $ML_{1+4}^{100^{\circ}C}$  12. The microstructures of the polymers were as in Example 1, i.e. of the "low cis" type.

#### EXAMPLES 10—17

These Examples, other than Example 10 which is a comparative Example, illustrate the effect of adding different amounts of additive to equivalent live polymeric solutions. The additive was cyanuril chloride and the monomer was 1,3-butadiene. Other conditions were as described in Example 1. The results are given in the Table.

Example No.	Cyanuryl chloride		Mooney Viscosity 100°C ML 1+4
	butyl lithium (initial) molar ratio	% conversion to polymer	
10	0	98	15
11	0.1	99	40.5
12	0.2	97	58
13	0.3	94	78
14	0.4	95	69
15	0.5	93	51
16	1	90	38
17	5	88	22

All polymers were rubbers and had similar microstructures to the products from Example 1.

- 5 Clearly, maximum coupling occurred between 0.2 and 0.3 cyanuryl chloride/butyl lithium (initial). Less than this amount of additive resulted in a smaller number of the active chains being coupled: more than this amount resulted in less coupling because with excess additive there is a decreased chance of one additive molecule reacting with 2 or 3 live chains.

#### EXAMPLE 18

- 15 The procedure of Example 1 was followed except that the additive was 2-chloropyrimidine in an amount given by the molar ratio 2-chloropyrimidine:butyl lithium (initial) = 1.0.

- 20 There was little increase in molecular weight as measured by change in Mooney Viscosity: the rubber had ML<sub>1+4</sub><sup>100°C</sup> 15 compared with a "blank" experiment (no additive) of ML<sub>1+4</sub><sup>100°C</sup> 12. The molecular weight as measured by osmometry were 105,000 (additive) and 103,000 (no additive).

- 25 The presence of the heteroaromatic ring as a terminal group was inferred from the fact that careful working-up of the polymer solution showed no pyrimidine residue in the acetone soluble portion. An equivalent mixture of short-stopped polybutadiene and chloropyrimidine in hexane/benzene was precipitated in methanol/acetone (1:10) in a similar way. By careful work-up, pyrimidine was detected in the acetone soluble portion.

- 30 The attachment of the heteroaromatic ring was verified by carrying out an identical experiment using 2-chloropyrimidine which had been labelled with C<sup>14</sup> in the heteroaromatic

nucleus. The rubber was radioactive emitting weak  $\beta$  radiations which did not decrease significantly upon extraction with refluxing acetone.

#### EXAMPLE 19

A very low molecular weight, liquid polybutadiene was made by adding over 4 hours at 20°C 50g. of a 15% w/w solution of 1,3-butadiene in hexane to a hexane solution of butyl lithium contained in a crown-capped glass pressure bottle. The final ratio (molar) of butadiene:butyl lithium was 4:1. The contents of the bottle containing 40g. of butadiene oligomer was heated for 4 hrs. at 50°C to complete the polymerisation.

At this stage a solution (0.5% w/w in benzene) of 2-bromoquinoline was added by syringe so that the molar ratio 2-bromoquinoline:butyl lithium was 1.0:1.0 and the contents of the bottle agitated. The appearance of the contents changed from transparent to opalescent as the reaction proceeded.

After 1 hour at 50°C antioxidant was added as before and the contents of the bottle poured into methanol. The molecular weight of the liquid polybutadiene was 560 compared with 430 for an identical experiment without additive. This confirmed that one end group per molecule had been added. Ultraviolet spectroscopy clearly showed the presence of a heteroaromatic ring in the polymer.

#### WHAT WE CLAIM IS:—

1. A method for increasing the molecular weight of conjugated diene homopolymers or copolymers prepared from monomers containing not more than 0.2% by weight of acetylenic or allenic impurities by means of an organometallic catalyst containing a metal of Group IA or IIA of the Periodic Table, comprising adding to the live polymerisation system one or more heteroaromatic compounds each containing at least one labile atom or group,

- as hereinbefore defined, the molar ratio of the heteroaromatic compound to the organometallic catalyst lying within the range 0.01—10.
- 5     2. A method as claimed in claim 1 wherein the organometallic catalyst is present in an amount of 0.01—10 parts per hundred parts by weight of total monomer.
  - 10    3. A method as claimed in either one of claims 1 and 2 wherein the organometallic catalyst is present in an amount of 0.01—1 part per hundred parts by weight of total monomer.
  - 15    4. A method as claimed in any one of claims 1 to 3 wherein the organometallic catalyst comprises n-butyl lithium, phenyl lithium, benzyl lithium, dilithium naphthyl, isopropyl potassium, phenyl sodium, diethyl magnesium or diethyl beryllium.
  - 20    5. A method as claimed in any one of the preceding claims wherein the heteroaromatic compound(s) contain(s) at least one heteroatom selected from sulphur, oxygen and nitrogen.
  - 25    6. A method as claimed in any one of the preceding claims wherein the at least one labile atom or group is selected from halogen alkoxy and aryloxy groups.
  - 30    7. A method as claimed in any one of the preceding claims wherein the heteroatom(s) in the or each heteroaromatic compound is/are nitrogen atom(s), and the labile atom(s) is/are halogen atoms.
  - 35    8. A method as claimed in any one of claims 1 to 6 wherein the heteroaromatic compound(s) is/are selected from 2,4,6-trichloropyridine, 2,4,6-tribromopyridine, 2,4,6-triiodopyridine, 2,4,6-triethoxypyridine, 1,3,6-tribromoisoquinoline, 2,4,5-tribromoquinoline, 3,4,5-trichloropyridazine, 2,4,6-trichloropyrimidine, 2,3,6-triethoxypyrazine, 2,5,6-tribromopyrazine, 2,3,6-trichloroquinoxaline, 2,4,6-trichlorotriazine-1,3,5 and 2,4,5-trichloroimidazole.
  - 40    9. A method as claimed in any one of claims 1 to 6 wherein the heteroaromatic compound is 2,4-dichlorothiazole and/or 2,5-diiodofuran.
  - 45    10. A method as claimed in any one of claims 1 to 6 wherein the heteroaromatic compound contains one labile atom or group only.
  - 50    11. A method as claimed in claim 10 wherein the heteroaromatic compound is 2-chlorothiazole and/or 2-bromopyrazine.
  - 55    12. A method as claimed in any one of the preceding claims wherein the conjugated diene homopolymers are formed from monomers having 4—8 carbon atoms in the main chain.
  - 60    13. A method as claimed in claim 12 wherein the monomers comprise 1,3-butadiene, isoprene, piperylene, methyl pentadiene and phenyl butadiene.
  - 65    14. A method as claimed in any one of claims 1 to 11 wherein the conjugated diene copolymers are formed from diene monomers having 4—8 carbon atoms in the main chain and comonomers comprising polymerisable vinyl compounds.
  15. A method as claimed in claim 14 wherein the polymerisable vinyl compounds comprise styrene, vinyl naphthalene, vinyl anthracene, vinyl toluene or vinyl xylene.
  16. A method as claimed in any one of the preceding claims wherein the level of acetylenic and allenic impurities is less than 500 ppm based on the weight of diene monomer.
  17. A method as claimed in any one of the preceding claims wherein the temperature is maintained between  $-100^{\circ}\text{C}$  and  $+150^{\circ}\text{C}$ .
  18. A method as claimed in claim 17 wherein the temperature is maintained between  $-10^{\circ}\text{C}$  and  $+100^{\circ}\text{C}$ .
  19. A method as claimed in any preceding claim wherein the pressure is maintained between atmospheric pressure and 50 atmospheres.
  20. A method for increasing the molecular weight of conjugated diene homopolymers or copolymers substantially as described with reference to Examples 1 to 4.
  21. A method as claimed in any one of the preceding claims wherein the molar ratio of heteroaromatic compound to organometallic catalyst is substantially  $\frac{m}{n}:1$  where m is the number of metal-to-carbon bonds in the catalyst and n is the number of labile atoms or groups present in the heteroaromatic compound.
  22. A method as claimed in any one of claims 1 to 5 wherein the at least one labile group is selected from tertiary amine and cyanide groups.
  23. A method as claimed in either one of claims 21 and 22 wherein the heteroaromatic compound contains only one labile group.
  24. A method as claimed in claim 10 wherein the heteroaromatic compound is 2-chloropyrimidine.
  25. A method as claimed in claim 12 wherein the monomer comprises 2-chloroprene.
  26. A method as claimed in either one of claims 14 and 15 wherein the comonomers are present in amounts of up to 80% by weight on a total monomer weight basis.
  27. A method as claimed in any one of claims 14, 15, and 26 wherein the vinyl compounds are present in amounts of up to 50% by weight of the total monomers.
  28. A method as claimed in any one of claims 14, 15, 25, 26, and 27 wherein the vinyl compounds are present in amounts of 10—30% by weight of the total monomers.
  29. A method as claimed in any preceding claim wherein the addition of the heteroaromatic compound is made after at least 80% conversion of the monomer(s) has taken place.
  30. A method for increasing the molecular

weight of conjugated diene homopolymers or copolymers substantially as described with reference to any of Examples 5 to 9 and 11 to 19.

5 31. Polymers having increased molecular weight when made by the method claimed in any one of claims 1 to 20.

32. Polymers having increased molecular weight when made by the method claimed in any one of claims 21 to 30.

10 33. Polymers having active end groups

when prepared by the method claimed in either one of claims 10 and 11.

34. Polymers having active end groups when prepared by the method claimed in either one of claims 23 and 24. 15

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